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COATED POLYCARBONATE RESIN MOLDED OBJECT

(Hifuku Porikaboneto-kei Jushi Seikei Buppin)

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SPECIFICATION

I. Title of the Invention

Coated Polycarbonate Resin Molded Object

II. Claims

(1) A polycarbonate resin molded object with improved abrasion resistance in which

a composition comprising (a) a copolymer of alkoxysilyl-containing acrylic or/and vinyl monomers and another monomer copolymerizable with these monomers, (b) a curing catalyst and (c) a cross-linking agent is coated/cured to take it as a prime coat layer and

a composition comprising an organopolysiloxane containing colloidal silica is coated/cured to take it as a top coat layer.

(2) A coated polycarbonate resin molded object according to Claim 1 in which

the said composition comprising an organopolysiloxane containing colloidal silica is a composition comprising at least one selected from a group composed of the following (A) and (B), (C) and (D).

(A) one, two or more hydrolyzates selected from epoxy-containing silicon compounds expressed by a general formula (1)



(where R^1 is an epoxy-containing group, R^2 is a hydrogen atom or a $\text{C}_1 - \text{C}_5$ hydrocarbyl group, R^3 is a $\text{C}_1 - \text{C}_5$ hydrocarbyl, alkoxyalkyl group or a $\text{C}_1 - \text{C}_4$ acyl group, α is 1 - 3, β is 0 - 2 and $\alpha + \beta \leq 3$,

(B) a hydrolyzate of organic silicon compound expressed by a general formula (2)

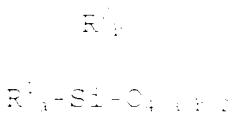


(where R^4 is a $\text{C}_1 - \text{C}_5$ hydrocarbyl, methacryloxy, amino, mercapto group, a fluorine- or chlorine-containing organic group, R^5 is a $\text{C}_1 - \text{C}_5$ hydrocarbyl, alkoxyalkyl group or a $\text{C}_1 - \text{C}_4$ acyl group, and α is 0 - 3.1,

(C) a colloidal silica and

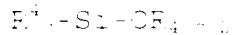
(D) a curing catalyst.

(3) A coated polycarbonate resin molded object according to Claim 2 in which the said organopolysiloxane containing colloidal silica is a composition comprising 100 pt (abbreviation of "pt" by weight, translator) of said hydrolyzate A' however, calculated as



by solid content),

56 - 550 pt of said hydrolyzate (B) (however, calculated as



by solid content),

4 - 334 pt of said colloidal silica (C) (however, calculated as SiO_2 by solid content), however, no more than 567 pt of (B) and (C) in total, and

said curing catalyst (D).

(4) A coated polycarbonate resin molded object according to Claim 3 in which the content of said (B) hydrolyzate is 105 - 430 pt, the content of said (C) colloidal silica is 16 - 200 pt, and the total of (B) and (C) is no more than 473 pt.

(5) A coated polycarbonate resin molded object according to Claim 1 in which the said (b) curing catalyst is a curing catalyst selected from organic acids, amines, metal acetylacetones and organic titanates.

(6) A coated polycarbonate resin molded object according to Claim 1 in which the said (c) cross-linking agent is a compound having at least two alcoholic hydroxyl groups in one molecule.

III. Detailed Description of the Invention

This invention relates to a coated polycarbonate resin molded object with excellent abrasion resistance which is made

in such a way that a prime coat with good adherence to a polycarbonate resin is coated/cured on the polycarbonate resin and a top coat containing a silicone resin is coated/cured thereon.

Generally, polycarbonate resins have been widely used as transparent plastic material because they are excellent in impact resistance and transparency, but the resins have such drawbacks that they are deficient in abrasion resistance and solvent resistance and is easily scratched on the surface as well as attacked by organic solvents. Various methods of coating with thermosetting resins have been proposed as methods for improving these drawbacks, but it is present situation that a fully satisfactory polycarbonate resin has not been obtained.

For example, a polycarbonate combining a trialkoxysilane such as methyltrialkoxysilane and phenyltrialkoxysilane, etc. with a tetraalkoxysilane such as ethyl silicate, butyl silicate, etc. or a mixture with other resin coatings, etc. have been known, but a polycarbonate with all of good abrasion resistance, hot water resistance, heat resistance, adherence and pot life of coating, etc. has not been obtained yet. Objects coated with coating compositions containing a curing catalyst, e. g., Lewis acids or their complexes such as BF_3 or BF_3 etherate in an epoxy-containing alkoxysilane, Brønsted acids such as HCl , HBr , HI , HNO_3 , HClO_4 , H_3PO_4 , etc., metal salts of organic acids such as

cobalt naphthenate, zinc naphthenate, etc. and then cured have been disclosed in Japan Tokkyo 53-15748, 53-35569, but the compositions are not practical because they have a short pot life of coating or take a long time in curing. Moreover, their adherence to polycarbonate substrate is poor. A coating composition based on colloidal silica and hydrolyzate of methyltrimethoxysilane has been disclosed in Japan Tokkyo 52-39691, this cured coating film has a sufficient hardness but is deficient in flexibility and is extremely difficult to give a good adherence to plastic substrate. Coating compositions containing a mixture of one, two or more selected from compounds containing both or one of epoxy group and silanol and/or siloxane group, a 1 - 100 μ m silica fine particle and an aluminum chelate compound have been disclosed in Japan Kokai 53-111336, but the hardness is insufficient and reduces due to boiling water immersion, etc. and also the adherence to bisphenol-type polycarbonate is poor for these cured coating films. Polycarbonate objects with a composition containing a thermosetting acrylic polymer and a UV absorptive compound as prime coat layer and a heat-cured colloidal

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silica-filled organopolysiloxane as top coat layer have been disclosed in Japan Kokai 56-92059, but they do not have very satisfactory adherence, hot water resistance, weather resistance, etc.

The inventors made earnest studies with the purpose of providing polycarbonate resin molded objects which remove such drawbacks and have improved abrasion resistance, solvent resistance, chemical resistance and weather resistance, consequently they discovered that the adherence of the top coat layer to a polycarbonate resin substrate can be improved by applying a prime coating containing an acrylic or vinyl copolymer with an alkoxysilyl group on a side chain, a curing catalyst and a cross-linking agent to the polycarbonate substrate and then baking to give a prime coat layer, and the abrasion resistance, solvent resistance, chemical resistance and weather resistance of polycarbonate resin molded objects can be improved by further applying a top coating comprising an organopolysiloxane containing colloidal silica to said prime coat layer and then baking.

Namely, this invention is to provide a coated polycarbonate resin molded object with improved abrasion resistance in which a composition comprising (a) a copolymer of alkoxysilyl-containing acrylic or/and vinyl monomers and another monomer copolymerizable with these monomers, (b) a curing catalyst and (c) a cross-linking agent is coated/cured to take it as a prime coat layer and a composition comprising an organopolysiloxane containing colloidal silica is coated/cured to take it as a top coat layer.

In this invention, the composition comprising a an organopolysiloxane containing colloidal silica used as the top coat is a composition comprising at least one selected from a group composed of the following (A) and (B), (C) and (D),

(A) one, two or more hydrolyzates selected from epoxy-containing silicon compounds expressed by a general formula (1)



(where R^1 is an epoxy-containing group, R^2 is a hydrogen atom or a $\text{C}_1 - \text{C}_6$ hydrocarbyl group, R^3 is a $\text{C}_1 - \text{C}_6$ hydrocarbyl, alkoxy-alkyl group or a $\text{C}_1 - \text{C}_4$ acyl group, a is 1 - 3, b is 0 - 2 and $a + b \leq 3$),

(B) a hydrolyzate of organosilicon compound expressed by a general formula (2)



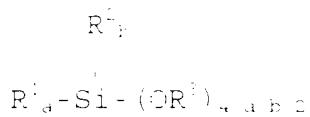
(where R^4 is a $\text{C}_1 - \text{C}_6$ hydrocarbyl, methacryloxy, amino, mercapto group, a fluorine- or chlorine-containing organic group, R^5 is a $\text{C}_1 - \text{C}_6$ hydrocarbyl, alkoxyalkyl group or a $\text{C}_1 - \text{C}_4$ acyl group, and c is 0 - 3.),

(C) a colloidal silica and

(D) a curing catalyst.

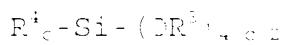
and is preferably a composition comprising

(A) 100 pt of one, two or more hydrolyzates selected from epoxy-containing silicon compounds expressed by the general formula (1) (however, calculated as



by solid content),

(B) 56 - 550 pt of a hydrolyzate of organosilicon compound expressed by the general formula (2) (however, calculated as



by solid content),

(C) 4 - 334 pt of a colloidal silica (however, calculated as SiO_2 by solid content), however, no more than 567 pt, preferably 60 - 567 pt of (B) and (C) in total, and

(D) a curing catalyst.

More preferably, the component (B) is 105 - 430 pt, the component (C) is 16 - 200 pt, and the total of component (B) and component (C) is 121 - 473 pt. If the total of component (B) and component (C) is less than 60 pt, the joint-use effect reduces; if it is more than 567 pt, the flexibility of cured coating film markedly reduces, and it becomes extremely difficult to give an improved adherence.

The following epoxy-containing silicon compounds of component A can be given as those used in this invention and shown by

the general formula (1). As specific examples of silicon compounds having one glycidoxy group,

glycidoxymethyltrimethoxysilane

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glycidoxymethyltriethoxysilane

β -glycidoxymethyltrimethoxysilane

β -glycidoxymethyltriethoxysilane

γ -glycidoxymethyltrimethoxysilane

γ -glycidoxymethyltriethoxysilane

γ -glycidoxymethyltri(methoxyethoxy)silane

γ -glycidoxymethyltriaacetoxysilane

δ -glycidoxymethyltrimethoxysilane

δ -glycidoxymethyltriethoxysilane

glycidoxymethyldimethoxysilane

glycidoxymethyl(ethyl)dimethoxysilane

glycidoxymethyl(phenyl)dimethoxysilane

glycidoxymethyl(vinyl)dimethoxysilane

glycidoxymethyl(dimethyl)methoxysilane

β -glycidoxymethyl(methyl)dimethoxysilane

β -glycidoxymethyl(ethyl)dimethoxysilane

β -glycidoxymethyl(dimethyl)methoxysilane

γ -glycidoxymethyl(methyl)dimethoxysilane

γ -glycidoxymethyl(ethyl)dimethoxysilane

γ -glycidoxypropyl(dimethyl)methoxysilane

δ -glycidoxypyethyl(methyl)dimethoxysilane

δ -glycidoxypyethyl(ethyl)dimethoxysilane

δ -glycidoxypyethyl(dimethyl)methoxysilane

As specific examples of silicon compounds having two or three glycidoxyl groups,

bis(glycidoxymethyl)dimethoxysilane

bis(glycidoxymethyl)diethoxysilane

bis(glycidoxylethyl)dimethoxysilane

bis(glycidoxylethyl)diethoxysilane

bis(glycidoxypropyl)dimethoxysilane

bis(glycidoxypropyl)diethoxysilane

tris(glycidoxymethyl)methoxysilane

tris(glycidoxymethyl)ethoxysilane

tris(glycidoxylethyl)methoxysilane

tris(glycidoxylethyl)ethoxysilane

tris(glycidoxypropyl)methoxysilane

tris(glycidoxypropyl)ethoxysilane

As specific examples of silicon compounds having a glycidyl group,

glycidylmethyltrimethoxysilane

glycidylmethyltriethoxysilane

β -glycidylethyltrimethoxysilane

β -glycidylethyltrimethoxysilane

γ -glycidylpropyltrimethoxysilane

γ -glycidylpropyltriethoxysilane

γ -glycidylpropyltri(methoxyethoxy)silane

γ -glycidylpropyltriacetoxysilane

As specific examples of silicon compounds having an alicyclic epoxy group,

3,4-epoxycyclohexylmethytrimethoxysilane

3,4-epoxycyclohexylmethytriethoxysilane

3,4-epoxycyclohexylethyltrimethoxysilane

3,4-epoxycyclohexylpropyltrimethoxysilane

3,4-epoxycyclohexylbutyltrimethoxysilane

can be given.

The following organosilicon compounds are given as those used in this invention and shown by said general formula (2) being the component (B). Namely, trimethylmethoxysilane, dimethyl-dimethoxysilane, methyltrimethoxysilane, tetraethoxysilane, phenyltrimethoxysilane, phenylmethyldimethoxysilane, vinyltriethoxysilane, vinyltri(β -methoxyethoxy)silane, vinyltriacetoxy-silane, γ -methacryloxypropyltrimethoxysilane, γ -aminopropyltriethoxysilane, N- β -aminethyl- γ -aminopropyltrimethoxysilane, N-bis(β -hydroxyethyl)- γ -aminopropyltriethoxysilane, N- β -aminoethyl- γ -aminopropyl methyl dimethoxysilane, γ -chloropropyltri-

methoxysilane, γ mercaptopropyltrimethoxysilane, 3,3,3 trifluoro-propyltrimethoxysilane, etc. are given. The organosilicon compounds may be used separately or by mixing two or more of them.

The colloidal silica of said component (C) is a colloid solu-

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tion given by dispersing an ultrafine silicic anhydride of preferably 1 - 100 μm in particle size in a dispersion medium, e.g., water or an alcoholic dispersion medium, it is produced and marketed by a well-known method.

The weather resistance of coating film is enhanced and the appearance and hardness after a weather resistance test is improved by joint use of these component (B) and component (C) with the component (A).

One, two or more hydrolyzates selected from epoxy-containing silicon compounds used as component (A) and expressed by said general formula (1) and one, two or more hydrolyzates selected from organosilicon compounds used as component (B) and expressed by said general formula (2) in this invention include those hydrolyzates in which a part or all of alkoxy, alkoxy-alkoxy or acyloxy groups are substituted by hydroxy groups and a part of the substituent hydroxy groups are naturally condensed with each other. As is well known, these hydrolyzates are obtained by hydrolysis in the presence of an acid in a mixed solvent like water-alcohol. When the silicon compounds expressed by said

general formulas (1) and (2) are used without hydrolysis, the cured coating film whitens and also has insufficient abrasion resistance.

When the silicon compounds expressed by said general formulas (1) and (2) are used as hydrolyzates, they give better results by mixing and co-hydrolysis simultaneously than separate hydrolysis in many cases.

The following catalysts can be used as curing catalysts of component (D) in the coating composition for top coat layer in this invention. Namely, ammonium perchlorate, ammonium nitrate, ammonium chloride, ammonium sulfate, ammonium thiocyanate, perchloric acid, hydrochloric acid, nitric acid, phosphoric acid, sulfuric acid, sulfonic acid, p-toluenesulfonic acid, boron trifluoride and their complexes with electronic donors; Lewis acids such as SnCl_4 , ZnCl_2 , FeCl_3 , AlCl_3 , SbCl_3 , TiCl_4 , etc. and their complexes; metal salts of organometallic acids such as sodium acetate, zinc naphthenate, cobalt naphthenate, zinc octylate, tin octylate, etc.; metal borofluoride such as zinc borofluoride, tin borofluoride, etc.; organic boric esters such as ethyl borate, methyl borate, etc.; alkalis such as sodium hydroxide, potassium hydroxide, etc.; titanic esters such as tetrabutoxytitanium, tetraisopropoxytitanium, etc.; metal acetyl-acetonate such as chromium acetylacetone, titanium acetylacetone, aluminium acetylacetone, cobalt acetylacetone,

nickel acetylacetone, etc.; amines such as n-butylamine, di-n-butylamine, tri-n-butylamine, dimethylbenzylamine, tris-2,4,6-dimethylaminophenol, guanidine, biguanide, imidazole, 1,5-diazabicyclo(4.3.0)nonene, 1,8-diazabicyclo(5.4.0)undecene-7, etc. and their salts; highly fluorinated aliphatic sulfonic salts such as ammonium trifluoromethylsulfonate, sodium trifluoromethylsulfonate, potassium trifluoromethylsulfonate, etc.; highly fluorinated aliphatic sulfonyl compounds such as $\text{NH}_4(\text{CF}_3\text{SO}_2)_2\text{CBr}$, $\text{K}(\text{CF}_3\text{SO}_2)_2\text{CH}$, $\text{Ba}[(\text{CF}_3\text{SO}_2)_2\text{CH}]_2$, etc. are given.

As curing catalysts which give good hardness and transparency, etc. of coating film and long pot life of coating solution among these curing catalysts, perchlorates, hydrochlorides, sulfates, carboxylates, amines and their salts, highly fluorinated aliphatic sulfonates and highly fluorinated aliphatic sulfonyl compounds represented by ammonium perchlorate, ammonium chloride, ammonium sulfate, ammonium nitrate, sodium acetate, imidazole and its salts, ammonium trifluoromethylsulfonate and bis(trifluoromethylsulfonyl)bromomethylammonium are suitable.

One, two or more of said various curing catalysts may be used together as curing catalysts contained in the composition for top coat in this invention. The amount of these catalysts is 0.05 - 10 wt%, preferably 0.1 - 5 wt% to the solid of coating composition for top coat.

As solvents which may be contained in the composition for top coat, alcohols, ketones, esters, ethers, cellosolves, halides, carboxylic acids, aromatic compounds, etc. can be given, and they can be used as mixed solvents of one, two or more of these solvents. Lower alcohols such as methanol, ethanol, propanol, isopropanol, butanol, etc.; cellosolves such as methyl cellosolve, ethyl cellosolve, butyl cellosolve, etc.; lower carboxylic acids such as formic acid, acetic acid, propionic acid, etc.; aromatic compounds such as toluene, xylene, etc.; esters such as ethyl acetate, butyl acetate, etc.; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, etc. are preferably used separately or as mixed solvents.

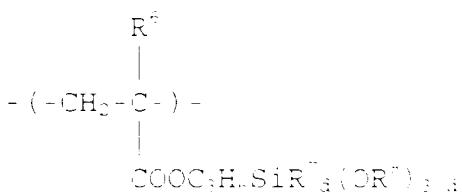
According to demand, a flow-controlling agent such as a fluorine surfactant, a block copolymer of alkylene oxide and dimethylsiloxane, etc. can be added to obtain a smooth coating film. A sufficient amount of these flow-controlling agents is as small as 0.01 - 5 wt%, preferably 0.03 - 3 wt% to the whole top coat composition. A small amount of antioxidant, UV absorbent, etc. can also be added.

The coating of above top coat is applied to a polycarbonate substrate precoated with a prime coat described later and baked

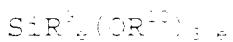
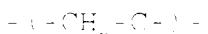
by commonly performed coating processes such as dipping process, spraying process, roller coating process or flow coating process, etc., then a coating film with good abrasion resistance, adherence, hot water resistance and weather resistance is obtained by baking for 20 min - 5 hr at a temperature of over 70°C and below the deformation temperature of substrate (e. g., 130°C) and then curing.

The preferable thickness of this top coating film is 1 - 30 µm, preferably 3 - 15 µm. If the thickness is less than 1 µm, the abrasion resistance is insufficient; if it becomes more than 30 µm, cracks easily occur.

In this invention, a copolymer of an acrylic or vinyl monomer having an alkoxy silyl group and another monomer copolymerizable therewith is a copolymer having a structure expressed by a general formula in its molecular structure.



(where R² is a hydrogen atom or methyl group, R³ is a C₁ - C₆ hydrocarbyl group, R⁴ is a C₁ - C₆ hydrocarbyl, alkoxyalkyl group or a C₁ - C₄ acyl group, and d is 0.1 or 2. R² may be same group or may be a mixed group of different groups' or/and a general formula



(where R^{β} is a $\text{C}_1 - \text{C}_6$ hydrocarbyl group, R^{β} is a $\text{C}_1 - \text{C}_6$ hydrocarbyl, alkoxyalkyl group or a $\text{C}_1 - \text{C}_6$ acyl group, and e is 0.1 or 2. R^{β} may be same group or may be a mixed group of different groups¹, and is obtained by addition polymerization of a monomer expressed by a general formula (3)



or/and a general formula (4)



(where R^{β} , R^{β} , R^{β} , R^{β} , R^{β} , d and e have above meanings). When R^{β} , R^{β} are mixed groups of different groups, a copolymer may be obtained by polymerization of monomers having different groups or may be obtained by polymerizing monomers having same group and then transesterification in the presence of an alcohol.

In acrylic monomers having an alkoxy silyl group expressed by the general formula (3), e. g., alkyl groups such as methyl, ethyl, propyl, butyl, etc.; aryl groups such as phenyl, etc.; alkenyl groups such as vinyl, allyl, etc. are given as R^{β} and alkyl

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groups such as methyl, ethyl, propyl, butyl, etc.; alkoxyalkyl groups such as methoxyethoxy, ethoxyethoxy, butoxyethoxy, etc.;

acyl groups such as acetyl, etc. are given as R^5 in the general formula (3); various compounds are used depending upon the kind of R^6 , R^7 , R^8 and the number of d in this invention, e. g., compounds as follows are given as specific examples. These compounds are γ -(meth)acryloxypropyltrimethoxysilane, γ -(meth)-acryloxy-propyltriethoxysilane, γ -(meth)acryloxypropylmethyldimethoxysilane, γ -(meth)acryloxypropylmethyldiethoxysilane, γ -(meth)acryloxypropyldimethylmethoxysilane, γ -(meth)acryloxypropyldimethylethoxysilane, etc.

In vinyl monomers having an alkoxy silyl group expressed by the general formula (4'), groups same as said R^7 are given as R^9 and groups same as said R^8 are given as R^{10} , and various compounds are used depending upon the kind of R^9 , R^{10} and the number of d in this invention, e. g., compounds as follows are given as specific examples. These compounds are vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(β -methoxyethoxy)silane, vinyltriacetoxysilane, vinylmethyldimethoxysilane, vinylmethyldiethoxysilane, vinyldimethylmethoxysilane, vinyldimethylethoxysilane, etc.

The following monomers are given as other monomers copolymerizable with the monomers expressed by the general formulas (3'), (4'). These monomers are methyl meth acrylate, ethyl meth acrylate, propyl meth acrylate, butyl meth acrylate,

? (several unreadable letters, translator) (meth)acrylate, ? (several unreadable letters, translator) (meth)acrylate, hydroxyethyl (meth)acrylate, butylene glycol mono(meth)acrylate, glycerol mono(meth)acrylate, polyethylene glycol mono(meth)-acrylate, polypropylene glycol mono(meth)acrylate, glycidyl (meth)acrylate, dimethylaminoethyl mono(meth)acrylate, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, dibutylaminoethyl (meth)acrylate, dimethylaminopropyl (meth)-acrylate, diethylaminopropyl (meth)acrylate, (meth)acrylamide, methylol (meth)acrylamide, (meth)acrylic acid, crotonic acid, maleic acid, itaconic acid, styrene, vinyltoluene, vinyl acetate, acrylonitrile, allyl alcohol, etc., but any monomers may be used if they are copolymerizable with the monomers expressed by the general formulas (3), (4).

1 - 70 wt%, preferably 2 - 40 wt% and more preferably 2 - 30 wt% of the monomers expressed by the general formulas (3), (4) are contained in the copolymers obtained by polymerization therewith. If the content is less than 1 wt%, the adherence with the prime coating film and the top coating film comprising an organopolysiloxane containing colloidal silica reduces; if it is more than 70 wt%, the adherence of said prime coating film to said polycarbonate resin substrate reduces and the stability of coating solution lowers.

The weight-average molecular weight of copolymer is 10,000 - 300,000, preferably 20,000 - 200,000. If the molecular weight is less than 10,000, the adherence to said polycarbonate resin substrate reduces; if it is more than 300,000, the appearance of coating film is harmed, thus these cases are undesirable.

As the curing catalysts used in the prime coating composition of this invention, Namely, inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, perchloric acid, etc.; organic acid such as formic acid, acetic acid, propionic acid, p-toluenesulfonic acid, oxalic acid, etc.; metal salts of organometallic acids such as zinc naphthenate, cobalt naphthenate, lead naphthenate, zinc octylate, tin octylate; amines such as n-butylamine, di-n-butylamine, diethanolamine, 3-triethoxysilylpropylamine, imidazoles, etc.; boron trifluoride and its complexes with electron donors; organic boric esters such as methyl borate, ethyl borate, etc.; organic titanates such as tetra-n-butoxytitanium and its oligomers, tetraisopropoxytitanium and its oligomers, diisopropoxybis(acetylacetone) titanium, di-n-butoxybis(triethanolamine) titanium, etc.; Lewis acids such as SnCl_4 , ZnCl_2 , FeCl_3 , AlCl_3 , SbCl_3 , TiCl_4 , etc. and their complexes; bicyclic amidines such as 1,5-diazabicyclo[4.3.0]nonene-5, 1,3-diazabicyclo[5.4.0]undecene-7, etc. and their salts; organotin compounds such as

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esters such as methyl borate, ethyl borate, etc.; organic titanates such as tetra-n-butoxytitanium and its oligomers, tetraisopropoxytitanium and its oligomers, diisopropoxybis(acetylacetone) titanium, di-n-butoxybis(triethanolamine) titanium, etc.; Lewis acids such as SnCl_4 , ZnCl_2 , FeCl_3 , AlCl_3 , SbCl_3 , TiCl_4 , etc. and their complexes; bicyclic amidines such as 1,5-diazabicyclo[4.3.0]nonene-5, 1,3-diazabicyclo[5.4.0]undecene-7, etc. and their salts; organotin compounds such as

dibutyltin dilaurate, dibutyltin maleate, etc.; quaternary ammonium salts such as tetramethylammonium chloride, triethylbenzeneammonium chloride, etc.; metal acetylacetonates such as chromium acetylacetone, titanium acetylacetone, aluminum acetylacetone, cobalt acetylacetone, nickel acetylacetone, etc. are given. In these curing catalysts, organic acids, amines, metal acetylacetones, organic titanates, etc. can be given as catalysts giving more excellent adherence to the polycarbonate resin substrate of coating film and a long pot life of coating solution.

One, two or more of the said various curing catalysts may be used together. The amount of curing catalysts is 0.01 - 10 wt%, preferably 0.1 - 5 wt% to said copolymer. If the amount is less than 0.01 wt%, the effect as curing catalyst is not found; if it is more than 10 wt%, the stability of coating solution lowers.

As cross-linking agents used in the prime coating of this invention, compounds having at least two alcoholic hydroxyl groups in one molecule such as ethylene glycol, propylene glycol, butanediol, hexanediol, neopentyl diol, diethylene glycol, triethylene glycol, glycerin, trimethylolpropane, pentaerythritol, dipentylerythritol, 1,4-cyclohexanedimethanol, hydrogenated bisphenol A and its ethylene oxide adduct; silane compounds such as methyltrimethoxysilane, methyltriethoxysilane,

dimethyldimethoxysilane, vinyltriethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -aminopropyltriethoxysilane etc. or their hydrolyzates; diisocyanates such as 2,6-tolylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, etc. are given, and compounds having at least two alcoholic hydroxyl groups in one molecule are most preferable among them. These cross-linking agents may be used separately or by combining two or more of them.

The amount of cross-linking agents is 0.1 wt% - 50 wt% to said copolymers, and the amount is more preferably decided so that the reactive groups (e. g., the alcoholic hydroxyl groups in the compounds having at least two alcoholic hydroxyl groups in one molecule) become 0.1 - 1.0 equiv., preferably 0.1 - 0.6 equiv.

Solvents and various additives are further added to the above components to make the composition into a prime coat.

As the solvents, alcohols such as methanol, ethanol, isopropanol, butanol, diacetone alcohol, etc.; ethers such as ethyl ether, ethylene glycol dimethyl ether, tetrahydrofuran, dioxane, etc.; cellosolves such as methyl cellosolve, ethyl cellosolve, isopropyl cellosolve, butyl cellosolve, etc.; esters such as ethyl acetate, butyl acetate, ethylene glycol diacetate, ethyl cellosolve acetate, etc.; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, diisopropyl ketone, etc.;

carboxylic acids such as formic acid, acetic acid, propionic acid, etc.; aliphatic hydrocarbons such as n-pentane, n-hexane,

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n-heptane, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, etc.; halogenated hydrocarbons such as dichloromethane, dichloroethane, trichloroethane, trichloroethylene, 1,1,2-trichloro-1,2,2-trifluoroethane, etc.; nitro compounds such as nitromethane, nitroethane, nitropropane, etc.; nitriles such as acetonitrile, propionitrile, butyronitrile, benzonitrile, etc.; amides such as formamide, acetamide, N,N-dimethylformamide, etc. can be given, and they may also be used by mixing.

Flow-controlling agent, UV absorbent, UV stabilizer, antioxidant, etc. can be given as additives.

As flow-controlling agents, commercial fluorine surfactants, block copolymers of alkylene oxides and dimethylenesiloxanes, etc. are given, 0 - 5 wt%, preferably 0 - 3 wt% of flow-controlling agents are used in the prime coat composition.

As UV absorbents, benzophenones such as 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-octoxybenzophenone, 2,4-hydroxybenzophenone, 2,2'-dihydroxy-4-methoxybenzophenone, etc.; benzotriazoles such as 2-(2'-hydroxy-2'-methylphenyl)benzotriazole, 2-(2'-hydroxy-2'-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-2'-octylphenyl)benzotriazole, 2-(2'-hydroxy-2',2'-di-t-butylphenyl)benzotriazole, 2-(2'-hydroxy-di-t-butylphenyl)-

benzotriazole, 2-(2'-hydroxy-di-t-butylphenyl)-5-chlorobenzotriazole, etc.; cyanoacrylates such as ethyl-2-cyano-3,3'-diphenyl acrylate, etc. are given, and 1 - 200 pt of UV absorbents are used in 100 pt of acrylic copolymers or vinyl copolymers in the prime coat composition.

A prime coating film is obtained by applying the prime coat composition comprising the above components to the surface of a polycarbonate resin molded object and then baking the resultant coating film at a temperature lower than the thermal deformation temperature of said resin molded object.

Application processes are commonly performed by dipping process, spraying process, roller coating process, flow coating process, etc., and the baking is carried out at 70 - 130°C for 20 min - 5 hr. A preferable thickness of said resultant prime coating film is 0.1 - 5 μ m, the solid content in the prime coat composition is regulated with aforesaid solvents in accordance with the application processes and conditions so as to obtain a desirable thickness, but the solid content of the prime coat composition is generally 1 - 20 wt%.

As polycarbonate resins applicable for this invention, e.g., bisphenol-type polycarbonate resins such as 4,4'-isopropylidenediphenol polycarbonate, etc., besides, other polycarbonates, diethylene glycol bisallyl carbonate, etc. described in USP

3,305,520 and [Polycarbonates] by Christopher and Fox, 161 - 175 (published in 1962), etc. are given..

The polycarbonate resins are used as various molded objects, e. g., spectacle lenses, ski goggles, door, automobile window, partition, etc.

The coating film layer of said coated polycarbonate resin molded objects based on this invention can be dyed or colored according to demand. Its dying process is carried out, for example, by dipping an object in a dyeing van, in which a common dispersion dye, a dispersant and a pH-regulating solution, etc. are added into water, at 85 - 95°C under a condition of 5 - 30 min. Thus, an dyed object with excellent abrasion resistance is obtained.

This invention will be illustrated in more detail by actual examples below, but this invention is not limited by these actual examples. "pt" and " " in the actual examples indicate "parts by weight" and "wt ", respectively.

Estimations of properties were performed by the following methods. Namely,

Abrasion resistance: It was judged by rubbing a sample with #0000 steel wool and examining the hardness of scratch as follows.

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A: not scratched even if rubbing strongly

B: little scratched if rubbing strongly

C: scratched even if rubbing weakly

Adherence: 11 parallel lines were drawn longitudinally and transversely at a spacing of 1 mm on the coating film surface with a knife and a cellophane adhesive tape was adhered thereon in a so-called cross-cut tape test, then the tape was peeled off, and the adherence was expressed by the number of non-peeled meshes in 100 meshes.

Hot water resistance: The state of a coating film after immersed for 1 hr in boiling water was examined.

Heat resistance: The state of a coating film after stored for 100 hr in a hot-air drying furnace of 120°C was examined.

Chemical resistance: The state of coating film after stored for 100 hr at room temperature in the following chemicals was examined.

3% sulfuric acid, 1% sodium hydroxide, 95% ethanol, acetone, ethyl acetate, carbon tetrachloride, toluene, n-heptane, 10% table salt water.

[Actual Example 1]

A top coating and a prime coating were prepared as follows, respectively.

(1) Preparation of top coating: 80 pt of γ -glycidoxypropyl-trimethoxysilane, 144 pt of methyltrimethoxysilane, 71 pt of a colloidal silica (Snowtex-C, solid content 20%, made by Nissan

Chemical Co., Ltd.) and 170 pt of 0.1 N aqueous hydrochloric acid solution were mixed and hydrolyzed at 80 - 85°C for 2 hr while refluxing.

The resultant solution comprised 12.2% of a hydrolyzate of γ -glycidioxypropyltrimethoxysilane calculated as $\text{CH}_2\text{-CH-CH}_2\text{-O-CH}_2\text{-Si-O}_{1.5}$, 15.3% of a hydrolyzate of methyltrimethoxysilane calculated as $\text{CH}_3\text{SiO}_{1.5}$ and 3.1% of colloidal silica calculated as SiO_2 .

73 pt of ethyl cellosolve, 1.3 pt of ammonium perchlorate and a little of a flow-controlling agent were added to 410 pt of the ternary hydrolyzate solution thus obtained to take it as a top coating.

(2) Preparation of prime coating: A solution dissolved with 1.0 pt of benzoyl peroxide in 200 pt of ethyl cellosolve was added in 2 hr to a mixture of 400 pt of ethyl cellosolve, 190 pt of ethyl methacrylate and 10 pt of γ -methacryloxypropyl trimethoxysilane while keeping it to 75°C in nitrogen atmosphere, and the mixture was further kept to same temperature for 6 hr. Subsequently, 1,486 pt of ethyl cellosolve, 2 pt of aluminum acetylacetone, 2.4 pt of 1,6-hexanediol and 20 pt of 2,4-dihydroxybenzophenone were added to take it as a prime coating.

This prime coating was applied to a polycarbonate substrate washed beforehand, then heated and dried at 130°C for 30 min in a hot-air drying furnace.

Next, the top coating prepared in said (i) was applied to the polycarbonate coated with the prime coating thus obtained, then heated, dried and cured at 130°C for 60 min in a hot-air drying furnace.

The coated polycarbonate resin molded object thus obtained was transparent, had abrasion resistance A, adherence 100/100, good hot water resistance and heat resistance as well as good abrasion resistance A and adherence 100/100 after a hot water test, respectively.

Moreover, the appearance, hardness and adherence were extremely good after 1,500 hr of a sunshine weatherometer test. The chemical resistance was good in any chemicals, and an abnormality in appearance after the test was not recognized.

[Comparison Example 1]

It was carried out similarly as Actual Example 1 except that a prime coating was prepared without using aluminum acetylacetone and 1,6-hexanediol in Actual Example 1. The coated polycarbonate resin molded object thus obtained was transparent, had abrasion resistance A, adherence 100/100, good

hot water resistance and heat resistance, but the adherence at 1,000 hr of a sunshine weatherometer test was 0/100.

[Comparison Example 2]

A solution dissolved with 1.0 pt of benzoyl peroxide in 200 pt of ethyl cellosolve was added in 2 hr to a mixture of 400 pt of ethyl cellosolve and 200 pt of ethyl methacrylate while keeping it to 75°C in nitrogen atmosphere, and the mixture was kept to same temperature for 6 hr. Subsequently 1,400 pt of ethyl cellosolve and 20 pt of 2,4-dihydroxybenzophenone were added to take it as a prime coat.

This prime coating was applied to a polycarbonate substrate washed beforehand, then heated and dried at 130°C for 30 min in a hot-air drying furnace.

Next, the top coating used in Actual Example 1 was applied to the polycarbonate coated with the prime coating layer thus obtained, then heated, dried and cured at 130°C for 60 min.

The coated polycarbonate resin molded object thus obtained was transparent, had abrasion resistance A, adherence 100/100, but the adherence after the hot water test was 0/100.

[Comparison Example 3]

A mixture of 100 pt of methyl methacrylate, 100 pt of ethyl methacrylate, 3 pt of methacrylic acid and 0.5 pt of azobisisobutyronitrile were added in 2 hr to 600 pt of butyl cellosolve

while keeping it to 100°C in nitrogen atmosphere, then the mixture was further kept to same temperature for 2 hr. Subsequently, 0.5 pt of azobisisobutyronitrile dissolved in 200 pt of butyl cellosolve was added at same temperature in 1 hr, then the mixture was further kept to same temperature for 3 hr. 32.0 pt of butyl cellosolve, 1 pt of hexakis(methoxy methyl) melamine, 0.06 pt of p-toluenesulfonic acid and 36 pt of 2,4-dihydroxybenzophenone were added to take it as a prime coating.

This prime coating was applied to a polycarbonate substrate washed beforehand, then heated and dried at 125°C for 30 min in a hot-air drying furnace.

Next, the top coating used in Actual Example 1 was applied to the polycarbonate coated with the prime coating layer thus obtained, then heated, dried and cured at 130°C for 60 min.

The coated polycarbonate resin molded object thus obtained was transparent, had abrasion resistance A, adherence 100/100, but the adherence after the hot water test was 0/100.

[Actual Example 2]

A top coating and a prime coating were prepared as follows, respectively.

(1) Preparation of top coating: 60 pt of γ -glycidoxypropyl-trimethoxysilane, 173 pt of methyltrimethoxysilane, 71 pt of a colloidal silica Snowtex-C, solid content 20%, made by Nissan Chemical Co., Ltd. and 190 pt of 0.1 N aqueous acetic acid

solution were mixed and hydrolyzed at 80 - 85°C for 2 hr while refluxing.

The resultant solution comprised 8.6% of a hydrolyzate of γ -glycidoxypropyltrimethoxysilane calculated as $\text{CH}_2\text{-CH}(\text{CH}_2\text{-O-C}_2\text{H}_5\text{-Si-O}_2\text{Si})_2$, 17.3% of a hydrolyzate of methyltrimethoxysilane calculated as $\text{CH}_3\text{SiO}_2\text{Si}$ and 2.9% of colloidal silica calculated as SiO_2 .

42 pt of ethyl cellosolve, 0.3 pt of ammonium perchlorate, 0.5 pt of ammonium chloride and a little of a flow-controlling agent were added to 450 pt of the ternary hydrolyzate solution thus obtained to take it as a top coating.

(2) Preparation of prime coating: A mixture of 160 pt of methyl methacrylate, 40 pt of γ -methacryloxypropyltrimethoxysilane and 2.0 pt of benzoyl peroxide was added to 300 pt of butyl cellosolve in 3 hr while keeping it to 100°C in nitrogen atmosphere, the mixture was further kept to same temperature for 3 hr and then 360 pt of ethylene glycol diacetate was added. 0.1

pt of p-toluenesulfonate, 1.0 pt of neopentyl glycol, 5.0 pt of 2-(2'-hydroxy-3'-octylphenyl)benzotriazole and 285 pt of butyl cellosolve were added to 215 pt of the copolymer thus obtained to take it as a prime coating.

This prime coating was applied to a polycarbonate substrate washed beforehand, then heated and dried at 130°C for 30 min in a hot-air drying furnace.

Next, the top coating prepared in said (1) was applied to the polycarbonate coated with the prime coating thus obtained, then heated, dried and cured at 130°C for 60 min in a hot-air drying furnace.

The coated polycarbonate resin molded object thus obtained was transparent, had abrasion resistance A, adherence 100/100, and abrasion resistance, adherence after a hot water test were also as good as A and 100/100, respectively. Moreover, the appearance, hardness and adherence were extremely good after 1,500 hr of a sunshine weatherometer test.

[Actual Example 3]

A prime coating was prepared as follows.

1.7 pt of cobalt naphthenate (containing 6% cobalt), 3.6 pt of trimethylolpropane, 20 pt of 2-hydroxy-4-methoxybenzophenone and 285 pt of butyl cellosolve were added to 215 pt of the

copolymer used for the prime coating of Actual Example 2 to take it as a prime coating.

This prime coating was applied to a polycarbonate substrate washed beforehand, then heated and dried at 120°C for 30 min in a hot-air drying furnace.

Next, the top coating prepared in Actual Example 2 was applied to the polycarbonate coated with the prime coating thus obtained, then heated, dried and cured at 130°C for 60 min in a hot-air drying furnace.

The coated polycarbonate resin molded object thus obtained was transparent, had abrasion resistance A, adherence 100/100, and abrasion resistance, adherence after a hot water test were also as good as A and 100/100, respectively. Moreover, the appearance, hardness and adherence were extremely good after 2,000 hr of a sunshine weatherometer test.

[Actual Example 4]

A top coating and a prime coating were prepared as follows, respectively.

(1) Preparation of top coating: 60 pt of γ -glycidoxypethyl-trimethoxysilane, 115 pt of methyltrimethoxysilane, 213 pt of a colloidal silica (Snowtex-C, solid content 20%, made by Nissan Chemical Co., Ltd.) and 5 pt of 1 N aqueous hydrochloric acid solution were added to 77 pt of isopropyl alcohol and hydrolyzed at 80 - 85°C for 2 hr while refluxing.

The resultant solution comprised 9.1% of a hydrolyzate of γ -glycidoxypropyltrimethoxysilane calculated as $\text{CH}_2\text{-CH-CH}_2\text{-O-C}_2\text{H}_5\text{-Si-OH}_3$, 12.1% of a hydrolyzate of methyltrimethoxysilane calculated as $\text{CH}_3\text{SiO}_2\text{H}_2$ and 9.1% of colloidal silica calculated as SiO_2 .

66 pt of ethyl cellosolve, 0.6 pt of sodium acetate and a little of a flow-controlling agent were added to 417 pt of the ternary hydrolyzate solution thus obtained to take it as a top coating.

(2) Preparation of prime coating: A mixture of 90 pt of methyl methacrylate, 10 pt of γ -methacryloxypropyltrimethoxysilane and 0.8 pt of azobisisbutyronitrile was added to 320 pt of n-butyl acetate in 2 hr while keeping it to 90°C in nitrogen atmosphere, the mixture was further kept to same temperature for 5 hr. Subsequently 760 pt of butyl cellosolve, 5 pt of a 10% aqueous di-n-butylamine solution, 1.1 pt of diethylene glycol and 20 pt of 2-(2'-hydroxy-5'-t-butylphenyl)benzotriazole were added to take it as a prime coating.

This prime coating was applied to a polycarbonate substrate washed beforehand, then heated and dried at 130°C for 30 min in a hot-air drying furnace.

Next, the top coating prepared in said (1) was applied to the polycarbonate coated with the prime coating thus obtained, then heated, dried and cured at 130°C for 60 min in a hot-air drying furnace.

The coated polycarbonate resin molded object thus obtained was transparent, had abrasion resistance A, adherence 100/100, and abrasion resistance, adherence after a hot water test were also as good as A and 100/100, respectively. Moreover, the appearance, hardness and adherence were extremely good after 1,500 hr of a sunshine weatherometer test.

[Actual Example 5]

It was carried out in all the same way as Actual Example 3 except that vinyltriethoxysilane was used in place of γ -methacryloxypropylmethyldimethoxysilane in the preparation of the prime coating of Actual Example 3.

The resultant coated polycarbonate resin molded object was transparent, and the abrasion resistance, adherence after the hot water test were A, 100/100, respectively. Moreover, the appearance, hardness and adherence were extremely good after 1,500 hr of a sunshine weatherometer test.

[Actual Example 6]

A top coating and a prime coating were prepared as follows, respectively.

(1) Preparation of top coating: 60 pt of γ -glycidoxypethyltrimethoxysilane, 86 pt of methyltrimethoxysilane, 213 pt of a colloidal silica (Snowtex-C, solid content 20%, made by Nissan Chemical Co., Ltd.), 30 pt of isopropyl alcohol and 35 pt of 0.1 N aqueous hydrochloric acid solution were mixed and hydrolyzed at 80 - 85°C for 2 hr while refluxing.

The resultant solution comprised 11.3% of a hydrolyzate of γ -glycidoxypethyltrimethoxysilane calculated as $\text{CH}_2\text{-CH-CH}_2\text{-O-CH}_2\text{-Si-O}_{1.5}$, 3.5% of a hydrolyzate of methyltrimethoxysilane calculated as $\text{CH}_3\text{SiO}_{1.5}$ and 6.5% of colloidal silica calculated as SiO_2 .

66 pt of ethyl cellosolve, 1.8 pt of 2-ethyl-4-methylimidazole and a little of a flow-controlling agent were added to 417 pt of the ternary hydrolyzate solution thus obtained to take it as a top coating.

(2) Preparation of prime coating: A solution dissolved with 1.0 pt of benzoyl peroxide in 200 pt of ethyl cellosolve was added in 2 hr to a mixture of 400 pt of ethyl cellosolve, 140 pt of ethyl methacrylate, 40 pt of glycidyl methacrylate and 20 pt of γ -methacryloxypropyl trimethoxysilane while keeping it to 75°C in nitrogen atmosphere, and the mixture was further kept to same temperature for 8 hr. Subsequently, 1,400 pt of ethyl cellosolve,

4 pt of tetraisopropoxytitanium and 1.4 pt of diethanolamine were added to take as a prime coating.

This prime coating was applied to a polycarbonate substrate washed beforehand, then heated and dried at 130°C for 30 min in a hot-air drying furnace.

Next, the top coating prepared in said (1) was applied to the polycarbonate coated with the prime coating thus obtained, then heated, dried and cured at 120°C for 60 min in a hot-air drying furnace.

The coated polycarbonate resin molded object thus obtained was transparent, and abrasion resistance, adherence after a hot water test were as good as A, 100/100, respectively. Moreover, the appearance, hardness and adherence were extremely good after 1,000 hr of a sunshine weatherometer test, but the adherence reduced to 80/100 after 1,500 hr.